

**Emission Factor Documentation for AP-42
Section 9.15**

Leather Tanning

Final Report

**For U. S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Emission Factor and Inventory Group**

**EPA Contract 68-D2-0159
Work Assignment No. 4-04**

MRI Project No. 4604-04

June 1997

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Research Triangle Park, NC 27711

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NOTICE

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PREFACE

This report was prepared by Midwest Research Institute (MRI) for the Office of Air Quality Planning and Standards (OAQPS), U. S. Environmental Protection Agency (EPA), under Contract No. 68-D2-0159, Work Assignment No. 4-04. Mr. Dallas Safriet was the requester of the work.

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EMISSION FACTOR DOCUMENTATION FOR AP-42 Section 9.15
Leather Tanning

1. INTRODUCTION

The document *Compilation of Air Pollutant Emission Factors* (AP-42) has been published by the U. S. Environmental Protection Agency (EPA) since 1972. Supplements to AP-42 have been routinely published to add new emission source categories and to update existing emission factors. AP-42 is routinely updated by EPA to respond to new emission factor needs of EPA, State and local air pollution control programs, and industry.

An emission factor is a representative value that attempts to relate the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant. Emission factors usually are expressed as the weight of pollutant divided by the unit weight, volume, distance, or duration of the activity that emits the pollutant. The emission factors presented in AP-42 may be appropriate to use in a number of situations, such as making source-specific emission estimates for areawide inventories for dispersion modeling, developing control strategies, screening sources for compliance purposes, establishing operating permit fees, and making permit applicability determinations. The purpose of this report is to provide background information to support preparation of AP-42 Section 9.15, Leather Tanning.

This background report consists of five sections. Section 1 includes the introduction to the report. Section 2 gives a description of the leather tanning industry. It includes a characterization of the industry, a description of the different process operations, a characterization of emission sources and pollutants emitted, and a description of the technology used to control emissions resulting from these sources. Section 3 is a review of emission data collection procedures. It describes the literature search, the screening of emission data reports, and the quality rating system for both emission data and emission factors. Section 4 details how the new AP-42 section was developed. It includes the review of specific data sets and a description of how candidate emission factors were developed. Section 5 presents the AP-42 Section 9.15, Leather Tanning.

2. INDUSTRY DESCRIPTION

2.1 INDUSTRY CHARACTERIZATION¹⁻⁵

Leather tanning is the process of converting raw hides or skins into leather. Hides and skins have the ability to absorb tannic acid and other chemical substances that prevent them from decaying, make them resistant to wetting, and keep them supple and durable. The surface of hides and skins contains the hair and oil glands and is known as the grain side. The flesh side of the hide or skin is much thicker and softer. The three types of hides and skins most often used in leather manufacture are from cattle, sheep, and pigs.

Tanning is essentially the reaction of collagen fibers in the hide with tannins, chromium, alum, or other chemical agents. The most common tanning agents used in the U.S. are trivalent chromium and vegetable tannins extracted from specific tree barks. Alum, syntans (man-made chemicals), glutaraldehyde, and heavy oils are other tanning agents. Vegetable tannins, aldehydes, oils, and most other tanning methods yield usable leathers from the tanning process alone. In chrome tanning, the reaction with the chromium salts gives a very stable hide fiber that is resistant to bacterial attack and high temperatures, but additional processes are usually performed to produce usable leathers.

There are approximately 111 leather tanning and finishing facilities in the United States. However, not every tannery may perform the entire tanning and finishing process. Figure 2-1 gives a breakdown of leather facilities by State. Leather tanning and finishing facilities are most prevalent in the northeast and midwest States, such as Pennsylvania, Massachusetts, New York, Michigan, and Wisconsin. The number of tanneries in the United States has significantly decreased in the last 40 years due to the development of synthetic substitutes for leather, increased leather imports, and environmental regulation. The total value of shipments for the industry (SIC 3111, Leather Tanning and Finishing) in 1992 was \$2.9 billion. Leather produced by domestic tanners is used to produce shoes, garments, upholstery, luggage, gloves, handbags, sporting goods, and a variety of other products.

2.2 PROCESS DESCRIPTION^{1-2,6-7}

Although the title of the AP-42 section is "Leather Tanning," the entire leathermaking process is considered here, not just the actual tanning step. "Leather tanning" is a general term for the numerous processing steps involved in converting animal hides or skins into finished leather. Production of leather by both vegetable tanning and chrome tanning is described below. Chrome tanning accounts for approximately 90 percent of U. S. tanning production. Figure 2-2 presents a general flow diagram for the leather tanning and finishing process. Trimming, soaking, fleshing, and unhairing, the first steps of the process, are referred to as the beamhouse operations. Bating, pickling, tanning, wringing, and splitting are referred to as tanyard processes. Finishing processes include conditioning, staking, dry milling, buffing, spray finishing, and plating.

2.2.1 Vegetable Tanning

Heavy leathers and sole leathers are produced by the vegetable tanning process, the oldest of any process in use in the leather tanning industry. The hides are received either salt cured or brine cured, and are trimmed and soaked usually overnight. The purpose of soaking is to remove salt and other solids and to restore moisture lost during curing so the hides will be able to absorb the tanning agents. Soaking may

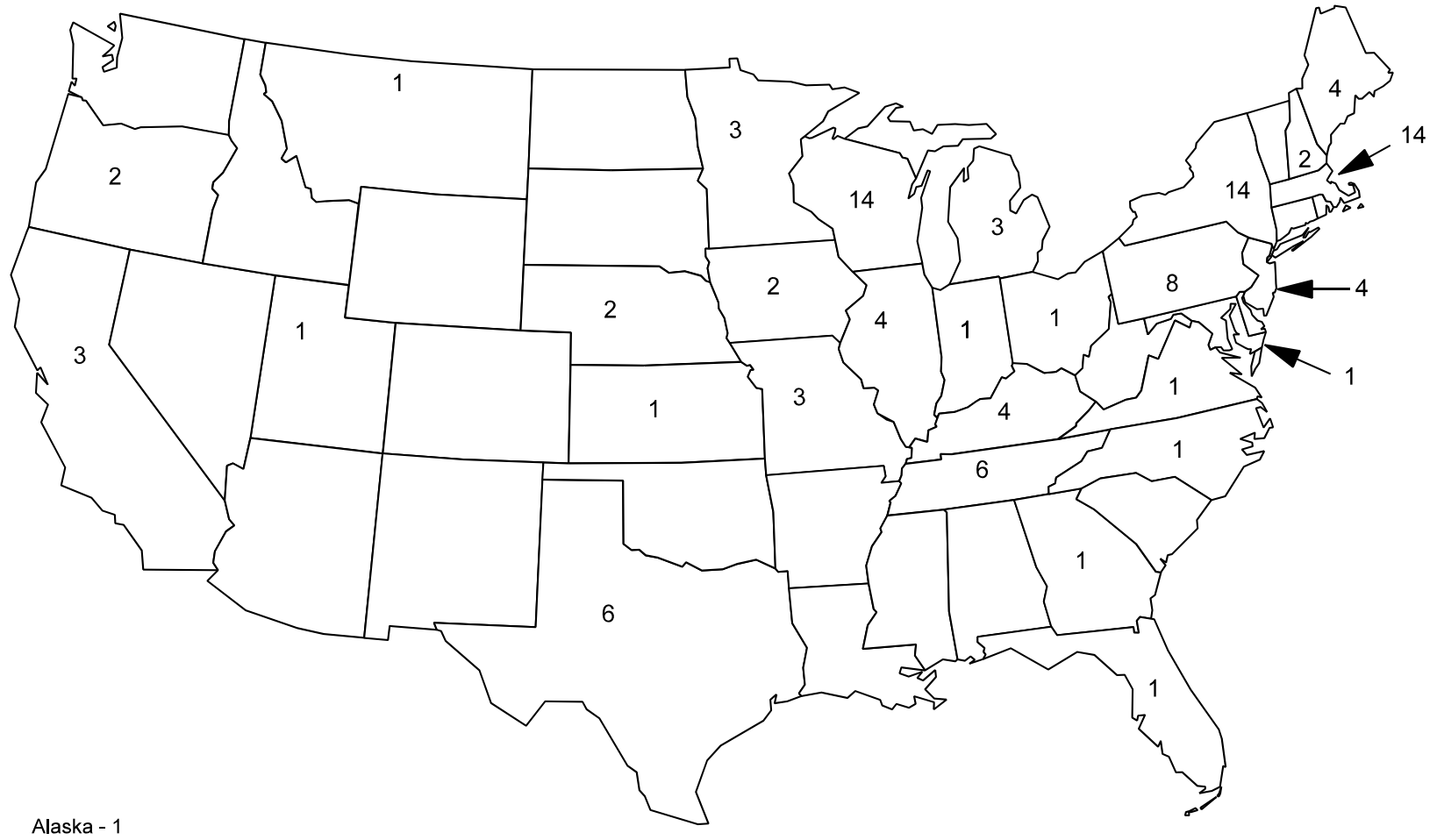


Figure 2-1. Leather facilities by State.⁵

be accomplished in drums, paddle vats, or pits. Following the soaking, the hides are fleshed to remove the excess tissue. Fleshing is necessary to impart uniform thickness and remove muscles or fat adhering to the hide.

Hides are then dehaired to ensure that the grain is clean and the hair follicles are free of hair roots. Liming is the most common method of hair removal, but thermal, oxidative, and chemical methods also exist. The normal procedure for liming, which may take several days, is to use a series of pits or drums containing lime liquors (calcium hydroxide) and sharpening agents, such as sodium sulfhydrate and sodium sulfide. The hair loosening process begins in the first bath, but the procedure may take several days. After removal from the last lime bath, the hides are ready for dehairing by scraping or by machine.

The liming process loosens the hair and other epidermal structures, and cleans, loosens, and expands the dermal fiber network. The concentration of chemicals, water temperature, and amount of agitation directly affect the rate at which hair is removed. The hair is sometimes recovered, cleaned, and sold.

The hides are then delimed and bated. Deliming is performed to solubilize the absorbed calcium hydroxide and lower the pH so the skins become receptive to the vegetable tanning without precipitation of the vegetable tannins in or on the skin. Bating is an enzymatic action for the removal of unwanted hide components (globular proteins, epidermis, hair) after liming. Bating also serves to impart softness, stretch, and flexibility to the leather. Bating and deliming are usually performed together by placing the hides in a solution of an ammonium salt and proteolytic enzymes at a water temperature of about 27° to 32°C (80° to 90°F).

When bating is complete, the hides are washed and substances that have been loosened or dissolved are removed. Pickling may also be performed by treating the hide with a salt and an acid to adjust the pH for preservation or tanning; the acidic environment is essential for tanning. Pickling commonly uses a brine solution and sulfuric acid.

Following pickling, the hides are ready for tanning. In the vegetable tanning process, a series of rockers is usually employed in which the concentration of the tanning materials starts low and is gradually increased as the tannage proceeds. A gentle rocking action keeps the hides in constant motion in the tanning solutions without folding or flexing. It usually takes three weeks for the tanning material to penetrate to the center of the hide. The vegetable tannins come from the bark and wood of several trees, such as quebracho, mangrove, hemlock, and mimosa. Vegetable tanning results not only in the preservation of the hide fiber but also in building characteristics such as fullness, body, and softness into the fiber. Vegetable tanned leather is light to dark brown in color.

The skins or hides are removed from the rockers, wrung, and may be cropped or split. Heavy hides may be retanned and scrubbed. In production of sole leather, the hides are commonly dipped in vats or drums containing sodium bicarbonate or sulfuric acid for bleaching and removal of surface tannins. The hides are then sent to an oil wheel, where materials such as lignosulfate, corn sugar, oils, and specialty chemicals are added to the leather. Alternatively, the leather may be soaked in an oil emulsion. The leather is then set out to smooth and dry. Setting out is the application of a stroking pressure from one end of a piece the other to remove further moisture and flatten creases.

After drying, the skins are wet again, piled down (piled flat on top of each other), and more oil may be added to the grain surface. For sole leather and similar uses, the leather is then rolled to compress

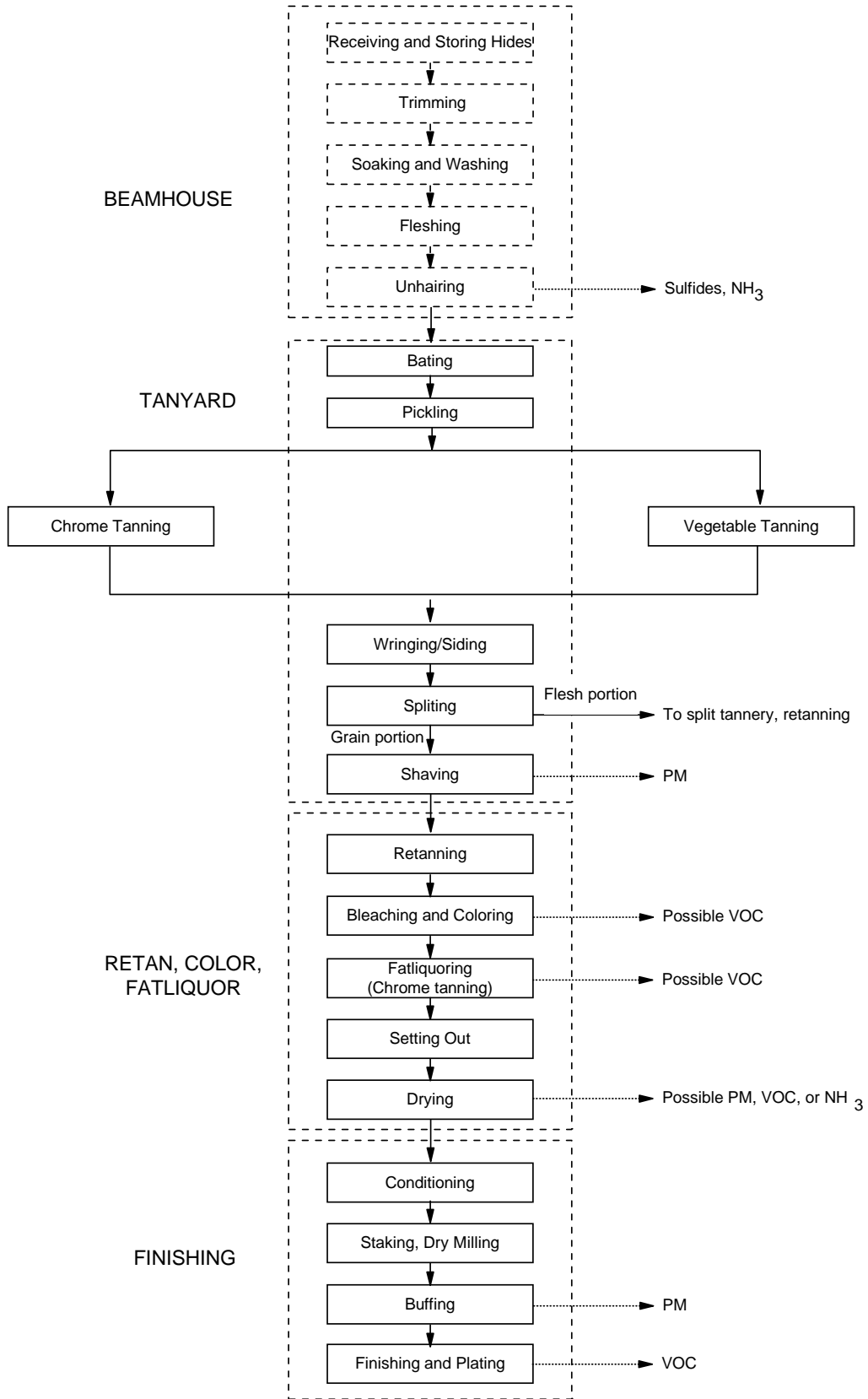


Figure 2-2. General flow diagram for leather tanning and finishing process.

fibers. The leather may be wet, dried, and rolled several times until it achieves the right degree of resiliency. Sole leather is then sponged with wax coating and dried, brushed, and dry-rolled. A high percentage of vegetable-tanned leather is sold without retanning, coloring, fatliquoring, or finishing.

2.2.2 Chrome Tanning

Chrome-tanned leather tends to be softer and more pliable than vegetable-tanned leather, has higher thermal stability, and is very stable in water. The chrome tanning process also takes less time than the vegetable tanning process. Almost all leather made from lighter-weight cattle hides and from the skin of sheep, lambs, goats, and pigs is chrome tanned. The first steps of the process (soaking, fleshing, liming/dehairing, deliming, bating, and pickling) are essentially the same as in vegetable tanning. However, in chrome tanning, the additional processes of retanning, dyeing, and fatliquoring may be performed to produce usable leathers. A preliminary degreasing process may be used for skins that are to be made into suede leather.

Chrome tanning in the United States is performed using a one-bath process and is usually carried out in drums. This process is based on the reaction between the hide and a trivalent chromium salt, usually basic chromic sulfate. In the typical one-bath process, the hides are in a pickled state at a pH of 3 or lower when the chrome tanning materials are introduced. The chrome tanning agent penetrates the hide and the pH is raised. This brings about changes in both the chromium salts and the protein in the hide and causes a reaction between them. When this reaction is complete, the leather is said to be full chrome tanned and has a light blue-green color. The balance of the many complex reactions involved and the control of the pH produces the quality of leather desired. Aluminum salts may also be incorporated into a chrome tannage for pretannage, and glutaraldehyde is sometimes used as a supplemental tannage in production of perspiration-resistant leathers. Two-bath chrome tannage is no longer performed in the U. S.

Chrome-tanned leather is piled down, wrung, and graded for the thickness and quality desired. The leather is then sent through machines that split it into flesh and grain layers. The sides are then shaved to the desired thickness with greater precision than that produced by the splitting machines. The flesh layers (known as splits) may be made into "rough buck" type shoe uppers, work gloves, heavy garment leathers, or finished and sold for shoe uppers. The grain leathers from the shaving machine are then separated for retanning, dyeing, and fatliquoring. Retanning is usually performed in a drum. Because of their bleaching effect on the bluish-green color of chromium tannage, syntans are typically used in the retanning step when white or pastel shades of leather are desired.

Leather that is not subject to scuffs and scratches may be dyed on the surface only. For other types of leather (i.e., shoe leather), the dye must penetrate further into the leather. Shades and degree of dye penetration are controlled by varying the pH, which affects the affinity of the dye for the leather fibers. In some cases in which the leather is to be finished, the dye gives a colored base so that scratches in the finish do not appear as undesirable blemishes. Typical dyestuffs are aniline-based compounds that combine with the skin to form an insoluble compound.

Fatliquoring is the process of introducing oil into the skin before the leather is dried. Oils and other fatty substances in fatliquors replace the natural oils lost in beamhouse and tanyard processes. Fatliquoring is usually performed in a drum using an oil emulsion at temperatures of about 60° to 66°C (140° to 150°F) for 30 to 40 minutes. After fatliquoring, the leather is wrung, set out, dried, and finished. The finishing process refers to all the steps that are carried out after drying.

Leather may be dried by any of five common methods. Air drying is the simplest method. The leather is hung or placed on racks and dried by the natural circulation of air around it. A toggling unit consists of a number of screens placed in a dryer that has controlled temperature and humidity. The leather is stretched and held in place by clamps. In a pasting unit, leathers are pasted on large sheets of plate glass, porcelain, or metal, with the grain surface to the flat sheet. The pasting plates are sent through a tunnel dryer with several controlled temperature and humidity zones. In vacuum drying, the leather is spread, grain down, on a smooth surface to which heat is applied. A hood is placed over the surface and a vacuum is applied to aid in drying the leather. The fifth method is high-frequency drying, which uses a high frequency electromagnetic field to dry the leather.

2.2.3 Leather Finishing

Leathers may be finished in a variety of ways: buffed with fine abrasives to produce a suede finish; waxed, shellacked, or treated with pigments, dyes, and resins to achieve a smooth, polished surface and the desired color; or lacquered with urethane for a glossy patent leather. Staking stretches and flexes the leather on automatic machinery to make the leather soft and pliable. Dry milling tumbles the hides in a large drum to flex and soften the leather. Buffing smooths and corrects irregularities in the grain surface by mechanical abrasion, and may be used on the flesh side to produce a suede nap. Water-based or solvent-based finishes may be applied to the leather, depending on the type and intended use. Plating, the final processing step, smooths the surface of the coating materials and bonds them firmly to the grain. Hides may also be embossed.

2.3 EMISSIONS^{2,4,8}

There are several potential sources of air emissions in the leather tanning and finishing industry. Emissions of VOC may occur during finishing processes if organic solvents are used. If organic degreasing solvents are used during soaking in suede leather manufacture, these VOC may also evaporate to the atmosphere. Emissions of VOC may also occur during other processes, such as fatliquoring and drying.

Ammonia emissions may occur during some of the wet processing steps (such as delimiting and unhairing) from breakdown of hide proteins, and may occur during drying if ammonia is used to aid dye penetration during coloring. Emissions of sulfides may occur during liming/unhairing and subsequent processes because sulfides, sulfates, and sulphydrates are used, especially in hair-destruction systems in which the hair is chemically removed from the hide. Also, alkaline sulfides in tannery wastewater can be converted to hydrogen sulfide if the pH is less than 8.0, resulting in release of this gas. Particulate emissions may occur during shaving, drying, and buffing.

Chromium emissions may occur from chromate reduction, handling of basic chromic sulfate powder, and from the buffing process. No air emissions of chromium occur during soaking or drying. At plants that purchase chromic sulfate in powder form, dust containing trivalent chromium may be emitted during storage, handling, and mixing of the dry chromic sulfate. The formulation process, however, is intermittent and short in duration, therefore lessening the potential chromium emissions. Further, the dry chromium sulfate is valuable and care is typically taken to minimize losses during handling and storage. The buffing operation also releases particulates, which may contain chromium. Leather tanning facilities, however, have not been viewed as sources of chromium emissions by the States in which they are located.

2.4 EMISSION CONTROL TECHNOLOGY⁴

Many tanneries are implementing water-based coatings to reduce VOC emissions. Control devices, such as thermal oxidizers, are less frequently used to reduce VOC emissions. Particulate emissions are controlled by dust collectors or scrubbers.

REFERENCES FOR SECTION 2

1. K. Bienkiewicz, *Physical Chemistry of Leathermaking*, Krieger Publishing Co., Malabar, FL, 1983.
2. *Development Document for Effluent Limitations Guidelines and Standards for the Leather Tanning and Finishing Point Source Category*, EPA-440/1-82-016, U.S. Environmental Protection Agency, Research Triangle Park, NC, November, 1982.
3. *1992 Census of Manufactures*, U.S. Department of Commerce, Bureau of Census, Washington, DC, April 1995.
4. Telecon, A. Marshall, Midwest Research Institute, with F. Rutland, Environmental Consultant, Leather Industries of America, August 7, 1996.
5. *1996 Membership Directory*, Leather Industries of America Inc.
6. M. T. Roberts and D. Etherington, *Bookbinding and the Conservation of Books, A Dictionary of Descriptive Terminology*.
7. T. C. Thorstensen, *Practical Leather Technology*, 4th Ed., Krieger Publishing Co., Malabar, FL, 1993.
8. *Locating and Estimating Air Emissions from Sources of Chromium*, EPA-450/4-84-007g, U.S. Environmental Protection Agency, Research Triangle Park, NC, July 1984.

3. GENERAL DATA REVIEW AND ANALYSIS PROCEDURES

3.1 LITERATURE SEARCH AND SCREENING

Data for this investigation were obtained from a number of sources within the Office of Air Quality Planning and Standards (OAQPS) and from outside organizations. The AP-42 background files located in the Emission Factor and Inventory Group (EFIG) were reviewed for information on the industry, processes, and emissions. The Factor Information and Retrieval (FIRE) data base was searched by SCC code for identification of the potential pollutants emitted and emission factors for those pollutants. Information on the industry, including number of plants, plant location, and annual production capacities, was obtained from the Census of Manufactures and other sources. In addition, the Leather Industries of America, the primary leather trade association, and the EPA Office of Water Programs were contacted for assistance in obtaining information about the industry and emissions. The EPA library was searched for additional test reports. Publications lists from the Office of Research and Development (ORD) and Control Technology Center (CTC) were also searched for reports on emissions from the leather industry.

To screen out unusable test reports, documents, and information from which emission factors could not be developed, the following general criteria were used:

1. Emission data must be from a primary reference:
 - a. Source testing must be from a referenced study that does not reiterate information from previous studies.
 - b. The document must constitute the original source of test data. For example, a technical paper was not included if the original study was contained in the previous document. If the exact source of the data could not be determined, the document was eliminated.
2. The referenced study should contain test results based on more than one test run. If results from only one run are presented, the emission factors must be down rated.
3. The report must contain sufficient data to evaluate the testing procedures and source operating conditions (e.g., one-page reports were generally rejected).

A final set of reference materials was compiled after a thorough review of the pertinent reports, documents, and information according to these criteria.

3.2 DATA QUALITY RATING SYSTEM¹

As part of the analysis of the emission data, the quantity and quality of the information contained in the final set of reference documents were evaluated. The following data were excluded from consideration:

1. Test series averages reported in units that cannot be converted to the selected reporting units;
2. Test series representing incompatible test methods (i.e., comparison of EPA Method 5 front half with EPA Method 5 front and back half);

3. Test series of controlled emissions for which the control device is not specified;
4. Test series in which the source process is not clearly identified and described; and
5. Test series in which it is not clear whether the emissions were measured before or after the control device.

Test data sets that were not excluded were assigned a quality rating. The rating system used was that specified by EFIG for preparing AP-42 sections. The data were rated as follows:

A—Multiple test runs that were performed using sound methodology and reported in enough detail for adequate validation. These tests do not necessarily conform to the methodology specified in EPA reference test methods, although these methods were used as a guide for the methodology actually used.

B—Tests that were performed by a generally sound methodology but lack enough detail for adequate validation.

C—Tests that were based on an unproven or new methodology or that lacked a significant amount of background information.

D—Tests that were based on a generally unacceptable method but may provide an order-of-magnitude value for the source.

The following criteria were used to evaluate source test reports for sound methodology and adequate detail:

1. Source operation. The manner in which the source was operated is well documented in the report. The source was operating within typical parameters during the test.

2. Sampling procedures. The sampling procedures conformed to a generally acceptable methodology. If actual procedures deviated from accepted methods, the deviations are well documented. When this occurred, an evaluation was made of the extent to which such alternative procedures could influence the test results.

3. Sampling and process data. Adequate sampling and process data are documented in the report, and any variations in the sampling and process operation are noted. If a large spread between test results cannot be explained by information contained in the test report, the data are suspect and are given a lower rating.

4. Analysis and calculations. The test reports contain original raw data sheets. The nomenclature and equations used were compared to those (if any) specified by EPA to establish equivalency. The depth of review of the calculations was dictated by the reviewer's confidence in the ability and conscientiousness of the tester, which in turn was based on factors such as consistency of results and completeness of other areas of the test report.

3.3 EMISSION FACTOR QUALITY RATING SYSTEM¹

The quality of the emission factors developed from analysis of the test data was rated using the following general criteria:

A—Excellent: Developed from A- and B-rated source test data taken from many randomly chosen facilities in the industry population. The source category is specific enough so that variability within the source category population may be minimized.

B—Above average: Developed only from A- or B-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industries. The source category is specific enough so that variability within the source category population may be minimized.

C—Average: Developed only from A-, B- and/or C-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. In addition, the source category is specific enough so that variability within the source category population may be minimized.

D—Below average: The emission factor was developed only from A-, B-, and/or C-rated test data from a small number of facilities, and there is reason to suspect that these facilities do not represent a random sample of the industry. There also may be evidence of variability within the source category population. Limitations on the use of the emission factor are noted in the emission factor table.

E—Poor: The emission factor was developed from C- and D-rated test data, and there is reason to suspect that the facilities tested do not represent a random sample of the industry. There also may be evidence of variability within the source category population. Limitations on the use of these factors are footnoted.

The use of these criteria is somewhat subjective and depends to an extent upon the individual reviewer. Details of the rating of each candidate emission factor are provided in Section 4.

REFERENCE FOR SECTION 3

1. *Procedures for Preparing Emission Factor Documents, Second Revised Draft Version*, Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Research Triangle Park, NC, September 1995.

4. REVIEW OF SPECIFIC DATA SETS

4.1 INTRODUCTION

This section describes the information that was evaluated to determine if pollutant emission factors could be developed for AP-42 Section 9.15, Leather Tanning.

4.2 REVIEW OF SPECIFIC DATA SETS

In addition to searching the FIRE and STIRS data bases, several EPA Regions and States (Pennsylvania, Massachusetts, New York, Wisconsin, Maine, and Michigan) were contacted to obtain emissions test reports for leather tanning facilities. Massachusetts, New York, and Maine had no air emissions information for leather tanning facilities. The State of Michigan sent copies of one facility's permit, but had no stack test information. The States of Wisconsin and Pennsylvania had emission inventory-type data (pounds of emissions and process type) but had no stack test data for leather tanning processes, only ancillary equipment, such as boilers.

Information on air emissions from leather tanning processes was limited to information supplied by the States; communication with the trade association's environmental consultant; the *Development Document for Effluent Limitations Guidelines and Standards for the Leather Tanning and Finishing Point Source Category*, EPA-440/1-82-016; and *Locating and Estimating Air Emissions from Sources of Chromium*, EPA-450/4-84-007g.

4.3 DEVELOPMENT OF CANDIDATE EMISSION FACTORS

No emission factors were developed for leather tanning because no source tests were found.

5. PROPOSED AP-42 SECTION

The proposed AP-42, Section 9.15, Leather Tanning, is presented on the following pages as it would appear in the document.